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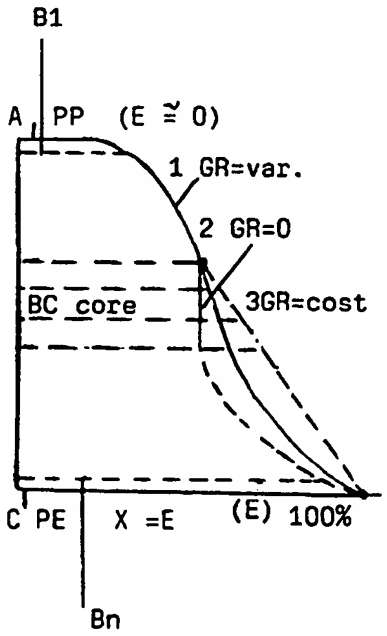
(54) Title: COEXTRUDED MULTILAYER FILMS FOR STERILIZABLE FLUID CONTAINERS

(57) Abstract

The films, foils, sheets and the like, flexible and transparent, fully formed of polyolefins, suitable in particular for the manufacture of infusional solution containers with the aid of forming, filling and sealing processes, comprise two terminal layers (A) and (C) of different polymeric composition, and "n" intermediate substrates B1, B2, ...Bi...Bn having gradients of ethylenic content and of softening temperature (fig. 1).



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COEXTRUDED MULTILAYER FILMS FOR STERILIZABLE FLUID CONTAINERS.

BACKGROUNG OF THE INVENTION

Field of the Invention.

The present invention concerns films, sheets, foils and similar flexible, transparent composites consisting of several coextruded layers having high inter-layers compatibility and adhesion, suitable, in particular, for the manufacture, by forming-filling-sealing processes (F-F-S), of containers especially of bags of fluids, particularly of infusional solutions which must be sterilized in autoclave with steam at about 121° C or more, and must have, besides transparency and good welding resistance, also high resistance to puncture and fall, said films comprising at least:

- an outer layer (A) which goes into contact with the soldering means during said F-F-S process and has melting temperature of at least 130° C and high mechanical strength to sustain the filled up container during the sterilization phase;
- an inner layer (C) which is destined to go in contact with said fluids and, once the container is formed and filled up, is responsable of the soldering hot or cold seals; and
- a complex intermediate layer (B) between (A) and (C) which is particularly important for the adhesion, transparency, mechanical resistance, shock absorption etc., said layer substantially consisting of olefin polymers in absence of adhesives and crosslinking compounds.

STATEMENT OF THE PRIOR ART

In patent application (Swiss Pat. Application N° 3771/93, corresponding

to EP-A-0658421) is described a multilayer coextruded film substantially of the above type, i.e. having the characteristics indicated as prior Art in the preamble of the present specification and relevant claim 1. In said Application (the description of which is intended to be herein incorporated), the outer layer (A) and the inner layer (C) had the same symmetrical composition (i.e. the same sterilizable polyolefin PO-STERI) whereas the intermediate layer (B), (not sterilizable, with melting point below 121° C and thickness from 50 to 200 microns) was constituted by polyolefins selected from the group consisting of thermoplastic polyolefins, ethylene-butene copolymers with density below 0.9g/m³ and relevant blends. The materials of layers (A and C) (having a thickness from 10 to 80 microns) were selected among: polymers and copolymers of propylene with ethylene and/or butylene; polymers or copolymers of ethylene with an alpha-olefin having six carbon atoms; relevant blends with or without minor amounts of elastomers. The following symbols will be used to indicate: PP, the propylene polymers and PE the ethylene polymers which can be linear (L) and have low (L), medium (M) or high (H) density (D).

In the examples layers (A) and (C) were both and contemporaneously PP or C8-LLDPE (linear, low density polyethylene with small amount of octene, (8)) whereas (B) could be also polyolefinic recovered and regranulated material. Similarly in EP-A-0216506 (classified X i.e. considered relevant in the Search Report of said EP-A-0658421) medical bags are described which are formed by laminates consisting of layers (A) and (C) both equal and selected among LDPE, HDPE or ethylen-alpha olefin copolymers with a density of at least 0.920g/cm³ whereas (B) is an ethylen-alpha olefin copolymer having

density below 0.935g/cm^3. The necessity of having layers (A) and (C) of symmetrical composition was, in general, attributable to the fact that, in so doing, were reduced the difficulties of the intermediate layer (B) to confer adeguate compatibility and adhesions between said layers (A) and (C) which just because they had a same coposition were already compatible.

The experience has however demonstrated thet it is neither easy nor sure to confer with a sole layer (even if very thick) of the material of (B) adequate adhesion, particularly after sterilization, to layers (A) and (C) notwistanding their equal composition. Indeed in the case of infusional solution pouches the problems to face are two-fold and concern not only the evaluation and selection of the (A) and (C) couples more suitable, for instance, in terms of viscosity, but also the problems in terms (f.i.) of the acceptability by the "PHARMACOPEA" for which interlayer adhesion values are to be respected which must be very high and critical, indispensable to guarantee an acceptable behaviour of the structure. There is moreover the current request of bags with always increasing solution volume, which must therefore show resistance characteristics adequately higher.

SUMMARY OF THE INVENTION

The main object of the present invention is that of providing coextruded films and relevant containers having a "maximum maximorum" of characteristics in particular an optimal combination of excellent values: of the adhesion between terminal layers (A) and (C) of different composition; of the compatibility, transparency, softness, fall resistance, seal strenght, absence of transfer of decomposition products in the solutions etc.

This and other objects are reached with the films and related containers

having the features recited in the claims. It has indeed been found that by advantageously using layers (A) and (C) of different composition and, between them, a discreet series of substrates B1, B2...Bn critically distributed with gradients as well of their content of combined monomeric ethylene (E) units, as of their melting (softening) temperature, it is possible to obtain films and bags able to satisfy even the most impellent exigencies f.i. of resistance, machinability, presentation etc., in addition to the Pharmacopea specific requirements.

BRIEF DESCRIPTION OF THE DRAWINGS

The different aspects and advantages of the invention will more clearly appear from the following description made with reference to both the examples and the accompanying drawing in which:

Fig. 1, is a schematic cross section of a multilayer film according to the invention, and Figures 2 and 3 are diagramms which emblematically represent the spatial variation of the ethylene contents, respectively of the melting temperatures in the various layers.

Description of the preferred embodiments.

Just to fix immediately the ideas, in Fig. 1 a composite film is represented which comprises, according to a first feature of the invention, two terminal layers (A) and (C) asymmetrical, i.e. of different composition (and characteristics) and a discreet number of "n" intermediate substrates B1, B2...Bi...Bn-1, Bn having gradients of ethylene content and of melting or softening temperature (Tfr).

According to an other preferred feature of the invention:

- a subnumber "mc" of the central substrates B1...Bmc virtually forming a

nucleous or core CO has the minimum softening temperature and gradients of E-content and of softening temperatures minimum or even null;

- a subnumber "ms" of substrates from B1 to Bms which virtually form an upper nucleus Bs show increasing ethylene contents and melting temperatures decreasing from the maximal temperature (Tmax) of (A) (about 140°C) till the minimal temperature (Tmin) lower than the sterilization temperature (121° C Tster);
- a subnumber "mi" of substrates located under the substrates of the core CO showing still increasing ethylene contents and softening temperatures also increasing from the above mentioned minimum temperature (Tmin; below 121° C) to the layer (C) temperature (Tc at least equal to the sterilization temperature Tster i.e. 121°C). Obviously, ms + mc + mi = n.

In Fig. 2 are represented the terminal layers (A), (C) and the intermediate layer (B) consisting of a sequence of sublayers (B1, B2...Bn).

Layer (A) consists substantially of combined monomeric units of propylene, possibly with minor quantities of ethylene; preferably (A) is selected between: PP homopolymers with PE low content; in border-line case, it could be also HDPE in admixture with block copolymers PP-PE; layer C consists substantially of ethylene combined units possibly with minor quantities of alpha-olefins; preferably C is selected between: LLDPE preferably in the form of copolymer with an alpha-olefin mainly octene and, subordinatively, butene, hexene; blends of said LLDPE and a LDPE prepared with high pressure process.

The central layer B, i.e. the sequence of sublayers (B1, B2...Bn) must show a high affinity with the terminal layers (i.e. A" and C") to assure a

perfect compatibility and adhesion of the whole structure as well at high temperature as at ambient temperature. Only in this manner it is possible to reach a maximum of the structure mechanical characteristics (including the puncture-and fall-resistances) by involving all the layers in this function of sustain and stress absorption in particular of the deformation.

According to a further feature of the invention, the substrate number is as high as possible however they form preferably successive perfectly compatible couples; this allows to pass through successive stages from the PP kindred face (A) to the PE kindred face (C) by maintaining a perfect cohesion and trasparency.

In the practical experience it has been ascertained that if, on one hand, "n" cannot be infinite and, on the other hand, only one substrate of (B) is not sufficient to assure the optimal combination of desired characteristics, particularly satisfactory results begin to appear already with two, better, three substrates possibly repeated several times; with such repetitions one succeeds in creating the sequence of characteristics suitable to optimize the inter-layer adhesion and the homogeneity of the structure.

In said structure (here described with general terms) the parameters which can give an indication of the affinity of the materials present in the successive layers, are the ethylene content (CE) and the softening point even if other primary characteristics are of fondamental importance (cristallinity degree, morphology in the solid state, contact angle etc.). In the practice for the PP-PE copolymers particularly adapted to form the substrates, have been selected the products with increasing ethylene content and for the linear PE have been preferred the products with increasing

copolymeric content in order to reach an optimum of adhesion between the two terminals. It has been surprisingly ascertained that there is a good compatibility between the random copolymers richer of ethylene and the so called polyethylenes with very low densities (VLLDPE) and these blends can bring about the term of passage through the structure PP-similar and those more PE-akin. These blends, already obtainable through a simple physical mixing and a successive extrusion, are further improved by a preliminary phase of mixing on the molten mass compounding and are rendered more suitable to the above described use if added with synthetic elastomers such as the polymers SBS, SEBS and the like or with polyolefinic rubbers such as the PP-PE-EPDM copolymers. In the examples some of these structures are reported which have contributed to reach the desired characteristics of interlayer adhesion and of sealing strength, fall-and puncture-resistances, trasparency after steam sterilization and machinability requested for the specific use of flexible pouches.

As a further object of the invention concerns the coextruded multilayer structures, in the following examples are reported structures suitable to the planar-head coextrusion called "cast extrusion". Anyway the invention cannot be limited to this technique but can also be embodied by blow coextrusion followed by tubular quenching or sequential coextrusion from separate heads, which allows the extrusion in sucessive steps of different materials which, once cooled, are wound together as a single sheet.

Experimental part.

In one particularly simple embodiment, the structures of the invention have been realized on one cast-coextrusion line consisting of five mono-

screw extruders with indipendent controls, able to melt and feed with good precision up to five different materials with the desired reciprocal flows: the molten materials are then convoied, still separately, to a system layer parallelization and of stabilization of the desired sequences which feed then a flat die for the final formation of the sheet in a molten state.

At the exit of the screw die the sheet is quenched by contact with a rotary cylinder innerly flown by a cooling liquid, and the linear speed of the cylinder in respect to the speed of the outgoing molten mass from the screw die allows to control at will the multimayer structure thickness. The more external layers are possibly provided with sliding or antibloking conventional agents to improve the machinability of the pouches. With the film samples of the examples, pouches are conventionally formed and filled with infusional solutions and then are sterilized in autoclave at 121°C and counter-pressure of 2 bar per each total cycle (heating, sterilization and cooling) of 60 minutes. The following structures (particularly the simple structures summarized in Table 1) are manufactured at the same extrusion speed and by maintaining constant the total thickness of 200 microns. The main functional characteristics of the so obtained films are tested and valitated according to the conventional methods, 72 hours after the extrusion. The simple materials cited in the Table correspond to the following types and characteristics:

A) PP COPO: random copolymer PP-PE with ethylene content from 3 to 3.5, MFI (melt flow index) measured at 230°C comprised between 9 and 12; melting point 148-152°C. Typical commercial polymers are: BOREALIS RE 764 or DAPLEN KFC 2004;

B1) PP COPO of high ethylene (content): it is again question of a random PP-PE copolymer but with ethylene high content (7-10%), MFI at 230°C of 12, melting point of 132°C. Typical commercial product is DAPLEN MFC 2110 SB;

B2) PP compound: random copolymer with low ethylene content (lower than 15%) blended and homogenized with block copolymers of the type SEBS, EPDM. The elastomer content can be between 20 and 30% and the MFI at 230°C can be between 2 and 8. There is a version totally obtained in the polymerisation phase but with similar characteristics called ADFLEX C 200 F made by MONTELL Company.

B3) VLLDPE: linear polyethylene with very low density (about .900g/cm^3) generally obtained by copolymerizing ethylene with comonomers such as butene, hexene or other alpha-olefins, in the presence of stereospecific catalysts. The product utilized in these tests is "CLEARFLEX" CLDO commercialized by the Company "POLIMERI EUROPA" with a comonomer content below 20%, MFI at 190°C of 3 and melting point of 115°C.

C) LLDPE: linear polyethylene (analogous to the above VLLDPE) prepared by stereospecific polymerization of ethylene with small amounts (below 10%) of comonomers of the alpha-olefin type. In a preferred embodiment two further substrates B4 and B5 were added as follows:

B4) MDPE: medium density polyethylene prepared with a conventional process (high pressure) in autoclave and characterized by a relatively high density (d = 0.933g/cm^3) which imparts particular stiffness gifts to the film. MFI at 190°C = 2.5 - 3.5.

B5) LDPE: copolymer with butene or hexene at a parity of all other conditions.

As anticipated, optimal results are obtained by repeating, several times, substrates formed of couples like B1-B2, B2- B3, B3-B4 or of triples like B1-B2-B3, B2-B3-B4, B3-B4-B5 etc.

Comparative Examples.

In addition to the examples according to the invention, two products are reported in the Table, which have structures not corresponding to those of the invention, (examples 4 and 5) having thus poor properties to confirm that a particular composition is needed to reach the characteristics requested for the specific utilization with pouches.

In the diagrams of Figures 2 and 3 are emblematically represented the spatial variations (Y axis) of the content of ethylene combined monomeric units (E on axis X in Fig. 2), respectively of the melting-softening temperature (Tfr on axis X of Fig. 3). Significantly the variations of these two important parameters are more marked (stronger) in the two major zones A-As and C-Ci above and below the core CO in which, on the contrary, E and Tfr can vary even in a negligible measure. Gradients of E and Tfr are generally present in said major zones A-AS and C-Ci but they could be minimal or negligible in the central zone CO. In said Figures the odashed curves represent other possible laws of variations of E and Tfr.

From Fig. 2 appears that in the central zone BC the ethylene content E can be constant (curve 2, zero gradient = GR = 0) or linearly vary (curve 3, constant gradient GR = cost) or have no linear variations (variable gradient GR = var.). From the foregoing it will observed that numerous variations and modification may be effected without departing from the true spirit and scope of the novel concept of the invention.

TABLE 1

TEST	Outer Layer A	Intermed. Layer B1	Intermed. Layer B2	Intermed. Layer B3	Inner Layer C	Sealing Stregth Kg/15mm	Delaminat. Force Kg/15mm	Transparency
1	PP Copo high 55 my	PP Copo high ethylene 15 my	PP Compound/ VLLDPE 15 my	VLLDPE 20 my	LLDPE 95 my	4.5	2.1	good
2	PP Copo 60 my	PP Compound 25 my	PP Compound/ VLLDPE 25 my	MDPE 10 my	LLDPE 80 my	4.9	2	good
3	PP Copo 55 my	PP Copo high ethylene 25 my	PP Compound 20 my	VLLDPE 15my	LLDPE 70my	4	2	good
4	PP Copo 55 my	PP Copo high ethylene 25 my	PP Compound 20 my	MDPE 20 my	LLDPE 80 my	2.7	0.5	not good
5	PP Copo 55 my	PP Compound 65 my			LLDPE 80 my	2.6	1.1	not good

CLAIMS

1) Films, sheets, foils and similar flexible, transparent composites consisting of several coextruded layers having high inter-layers compatibility and adhesion, suitable, in particular, for the manufacture by forming-filling-sealing processes (F-F-S) of containers especially of bags of fluids, particularly of infusional solutions which must be sterilized in autoclave with steam at about 121° C or more, and must have, besides transparency and good welding resistance, also high resistance to puncture and drops, said films comprising at least:

- an outer layer (A) which goes into contact with the soldering means during said F-F-S process and has melting temperature of at least 130° C and high mechanical strength to sustain the filled up container during the sterilization phase;
- an inner layer (C) which is destined to go in contact with said fluids and, once the container is formed and filled up, is responsable of the soldering hot or cold seals; and
- a complex intermediate layer (B) between (A) and (C) which is particularly important for the adhesion, transparency, mechanical resistance, shock absorption etc., said layer substantially consisting of olefin polymers in absence of adhesives and crosslinking compounds;

characterized in that:

- layers (A) and (C) have heterogeneous compositions; layer (A) consisting substantially of a polymer formed of combined monomeric units of

propylene with possibly small proportions of combined monomeric units of ethylene or alpha-olefins; layer (C) consisting substantially of combined units of ethylene with possibly small proportions of alpha-olefins; and layer (B) consisting of a discreet number (n) of substantially polymeric layers comprising a number "ms" of substrates in the upper part (A-AS) near (A), a number "mc" of central substrates forming a central nuleus or core (BB) of the intermediate layer (B) between (A) and (C), and a number "mi" of layers in the lower part C-Ci comprised between said ensembles B-Bc and C-Ci, wherin ms + mi + mc = n, at least the layers or substrates "ms" and "mc" of the upper (A-As) and lower C-Ci parts, respectively, having gradients of the ethylene combined monomeric unit content and of the softening temperature.

2) Films according to claim 1, characterized in that outer layer (A) is formed substantially of combined monomeric units of propylene possibly with minor proportions of ethylene combined units not higher than 4%; layer (C) is formed substantially of combined monomeric units of ethylene possibly with minor proportions of an alpha-olefin; all the "ms" and "mc" substrates in the zones A-As and C-Ci of (B) showing: increasing contents of ethylene monomeric units but decreasing softening temperatures (Tfr) in A-As from the maximum softening temperature (Tmax) of (A) to the minimum temperature (Tmin) in the core (CO, BB), respectively increasing softening temperature in zone C-Ci from said core minimum temperature of layer (C) up to at least the sterilization temperature of 121° C.

3) Films according to claim 2, characterized in that "mc" is comprised

between 6 and 8, "ms" is equal to at least 2, and "mi" is comprised between 2 and 10.

4) Films according to at least one of the preceding claims, characterized in that layer (A) is selected from the group of propylene polymers having ethylene content lower than 3,5%, and has thicknesses between 10 and 80 microns, layer (C) is selected from the group of ethylene polymers having an alpha-olefin content lower than 10%, said "ms" upper substrates having melting temperatures decreasing from 140° C to about 90° C, said lower "mi" substrates having temperatures increasing from 90° C to at least 121° C.

5) Films according to at least one of the preceding claims, characterized in that: - layer (A) is formed of a random copolymer of PP (polypropylene) with a PE (polyethylene) content below 3,5; - layer (C) is a LLDPE (linear low density polyethylene) with an alpha-olefin content below 10%; - layer (B) comprises at least a first substrate B2 constituted of a compound of a random PP copolymer and of an elastomeric modifier selected among the terpolymers ethylene-propylene-monomeric diene EPDM or SEBS; and - the substrates B3, B4, B5, B6, B7 etc. are formed of polyethylenes selected among: VLLDPE and LDPE of the polymeric type having minor proportions of an alpha-olefin, and MDPE.

6) Composite multilayer films substantially according to Table 1.

7) Containers, particularly bags for fluids especially for medical solutions, sterilizable in autoclave with steam at 121° C or more, consisting of polyolefinic coextruded multilayer films, at least a layer of which has substrates showing softening temperatures below 121° C,

characterized in that the thicknesses of the outer (A) and inner (C) layers (which during the sterilization at 121° C or more, i.e. when at least a big portion of the "n" substrates of the intermediate layer (B) are in conditions of partial melting and impart mechanical resistance to the container), increase as the weight of the fluid contained in the bag and the total thickness of (B) increase, and are above 40 microns when the total thicknesses of (B) are above 50 microns and, for fluid quantities of at least 1 liter, the number "n" of the substrates of (B) also increasing as said last fluid quantity increases.

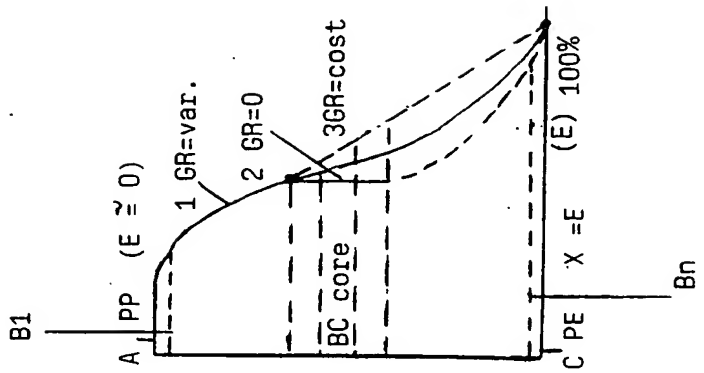

FIG. 3

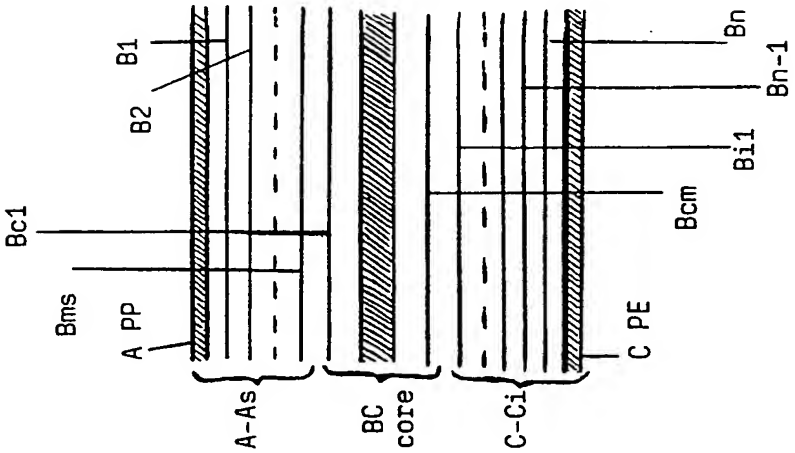

FIG. 2

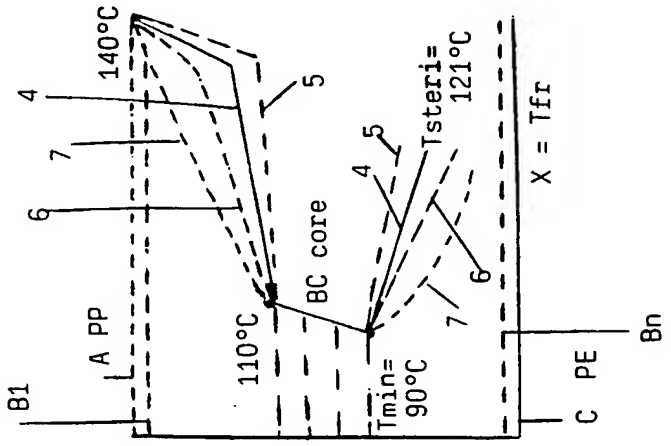

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/00204

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/32 B32B7/02 A61J1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B A61J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 739 713 A (FRESENIUS AG) 30 October 1996 see the whole document	1-7
A	EP 0 658 421 A (BIEFFE MEDITAL SA) 21 June 1995 cited in the application see the whole document	1-7
A	EP 0 564 206 A (TERUMO CORP) 6 October 1993 see claims; examples 22,23	1-7
A	EP 0 282 282 A (SUMITOMO CHEMICAL CO) 14 September 1988 see claims	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
29 May 1998	22/06/1998

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 309939 A (NIPPON PETROCHEM CO LTD), 26 November 1996, see abstract	1
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 100 (C-1030), 26 February 1993 & JP 04 288162 A (OZAKI KEIKAGAKU KK), 13 October 1992, see abstract	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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